

#### IN THE U.S. PATENT AND TRADEMARK OFFICE

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Applicants: Atsushi YABE et al

For: ELECTROLESS COPPER PLATING METHOD

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Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

## APPELLANTS' BRIEF ON APPEAL

Sir:

This is an appeal from a decision of the Examiner dated October 20, 2008, finally rejecting Claims 5 and 6.

# REAL PARTY IN INTEREST

Nikko Materials Co., Ltd. is the assignee of the present application and the real party in interest.

#### RELATED APPEALS AND INTERFERENCES

There are no related appeals and interferences to the present application.

#### STATUS OF CLAIMS

Claims 5 and 6 are pending and are the claims under consideration on appeal. Claims 1-4 have been canceled.

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## STATUS OF AMENDMENTS

The Amendment After Final Rejection dated January 16, 2009 has been entered.

#### SUMMARY OF CLAIMED SUBJECT MATTER

Appellants' invention, as defined in independent Claim 6, is directed to an electroless copper plating method which comprises the steps of preparing a pretreatment agent by reacting or mixing a noble metal compound and a silane coupling agent having a functional group with metal-capturing capability (paragraph [0021] of the present specification), pre-treating a mirror surface having a surface roughness of less than 10 nm with a pretreatment agent prior to electroless copper plating (paragraph [0011] of the present specification), performing electroless copper plating on the pretreated mirror surface with an electroless copper plating solution comprising a first reducing agent, hypophosphorus acid or a hypophosphite as a second reducing agent and a stabilizer for inhibiting copper deposition (paragraph [0012] of the specification), and forming a thin film having a thickness of no more than 500 nm on the pretreated mirror surface by the electroless copper plating (paragraph [0007] in the specification).

GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

Appellants respectfully request the review of the rejection of Claim 6 under 35 USC 103(a) as being unpatentable over Kondo et al in view of Uzoh et al, Maenosono and WO 01/49898 (WO '898). Appellants also respectfully request the review of the rejection of Claim 5 under 35 USC 103(a) as being unpatentable over Kondo et al in view of Uzoh, Maenosono and WO '898 and further in view of Yoshida et al and Verbunt.

## ARGUMENT

The present invention provides an electroless copper plating method which enables a uniform plating to be formed at

lower temperatures on a mirror surface, such as a semiconductor wafer. The present invention is based on the discovery that when a mirror surface having a surface roughness of less than 10 nanometers is treated with a pretreatment agent formed by reacting or mixing a noble metal compound and a silane coupling agent having a functional group with metal-capturing capability and the pretreated mirror surface electrolessly copper plated with an electroless copper plating solution comprising a first reducing agent, hypophosphorus acid or a hypophosphite as a second reducing agent and a stabilizer for inhibiting copper deposition, excessive deposition reactions are prevented, and a uniform plating is provided on the mirror surface having a surface roughness of less than 10 nanometers and a thin film can be formed having a thickness of no more than 500 nanometers. It is respectfully submitted that the prior art cited by the Examiner does not negate the patentability of the presently claimed invention.

# REJECTION OF CLAIM 6 UNDER 35 USC 103(a) OVER KONDO ET AL IN VIEW OF UZOH ET AL, MAENOSONO AND WO '898

The Kondo et al reference discloses an electroless copper plating solution containing a copper salt, a complexing agent for copper ion, a reducing agent and a pH-adjuster. An excess amount of trialkanolamine is added as the complexing agent for the copper ion and as an accelerator. The invention of this reference is based on the discovery that an increased copper deposition rate can be obtained by using a monoamine-type trialkanolamine as a complexing agent and as an accelerator in the electroless copper plating solution. The reducing agent used in the electroless copper plating solution is disclosed as not being particularly limited and formaldehyde and derivatives and precursors thereof such as paraformaldehyde are disclosed as being most suitable. This reference further discloses that other reducing agents can be used in

combination with formalin since formalin alone may be detrimental to the human body and cause instability of the bath when used in a large amount. To reduce the amount of formalin used in the plating solution, Kondo et al discloses that sodium hypophosphite can be added to the formalin but discloses in Figures 9 and 10 that the plating rate for formalin and sodium hypophosphite is almost equal to that of formalin alone. As such, this reference only teaches that sodium hypophosphate can be used as a partial substitute for formaldehyde and that no unexpected results or effects occur when sodium hypophosphite is combined with formaldehyde in the electroless copper plating solution disclosed there. It is also to be pointed out that Kondo et al has no disclosure with respect to the surface of the substrate being plated being a "mirror surface". In fact, column 7, lines 53 through 58 of this reference discloses that the article or substrate is pretreated, which means cleaned and chemically roughened, and catalyzed to make the substrate sensitive to copper deposition. Therefore, this reference does not disclose the provision of a substrate with a mirror surface having a surface roughness of less than 10 nm, the pretreatment of the mirror surface of the substrate with a pretreatment agent formed by reacting or mixing a noble metal compound and a silane coupling agent having a functional group with metalcapturing capability and the formation of a thin film having a thickness of no more than 500 nm on the pretreated mirror surface by electroless copper plating.

The Uzoh et al reference discloses a method and structure for reducing defects and integrated circuits and substrates. The method comprises the steps of depositing a seed layer having a consistent thickness over a barrier layer, electrodepositing a planer copper layer on the seed layer and subsequently electroetching it until a thinned seed layer remains over the filled regions. The Examiner states that this reference teaches that it is well known, when providing copper electroless plating, that it is desirable to overplate

substrates formed from silicon wafers. However, the only discussion this reference has with respect to electroless plating is a general discussion in the background of the invention which states that copper may be plated by electroless or electroplating techniques on a substrate. There is no specific disclosure in this reference regarding overplating substrates formed from silicon wafers by copper electroless plating. In fact, in this reference, all of the plating is performed by electroplating and not electroless plating. Additionally, since the primary Kondo et al reference is concerned with articles or substrates having a roughened surface, the teachings contained in Uzoh et al would not be transferred to Kondo et al by one of ordinary skill in the art.

The Maenosono reference discloses a support for a flexible magnetic recording medium made of a polyamide film obtained by coating a solution of a solvent-soluble polyamide resin on a solid substrate having a smooth surface, removing the solvent and then peeling apart a coated film from the substrate. In this reference, a polyamide solution is applied to a polished inorganic substrate having a center line roughness of no greater than 10 nm, the solvent evaporated to form the polyamide film and the film peeled from the substrate.

This reference has been cited by the Examiner as teaching that silicon wafers and other substrates with a roughness of no more than 10 nm are commonly coated by electrochemical deposition methods. However, the plating method disclosed in Maenosono is electrochemical deposition and not electroless plating as required by the presently claimed invention and the primary Kondo et al reference. Maenosono et al states in paragraph [0030] that the thin film is preferably made of a material that the resistance (adhesion) during peeling apart the polyamide film after the formation thereof is low. This means that the deposited thin layer of Maenosono is not desired to adhere to the substrate, which is opposite to that

of the present invention, and the previously cited references, where the plated thin layer is to stably bond to the surface of the substrate. The disclosure of Maenosono et al that a thin film of another material may be formed on a substrate having a high flatness and center line surface roughness of no more than 10 nm by electrochemical deposition does not suggest to one of ordinary skill in the art to combine this reference and the previously discussed two references since there is no expectation that Kondo et al's solution, which is designed to be used with a conventionally roughened substrate surface, would also be suitable for use with substrates having a mirror surface as required by Maenosono. Additionally, as discussed previously, since the Maenosono reference is directed to electrochemical deposition and not electroless plating to form the thin film on the surface of the substrate and then subsequently removing the deposited thin layer, the combination of Maenosono et al with Kondo and Uzoh et al does not even present a showing of prima facie obviousness under 35 USC 103(a).

WO '898 is directed to a method for metal plating which comprises a step of admixing or reacting a noble metal compound as a catalyst with a silane coupling agent containing a functional group having the capability of capturing a metal to prepare a pre-treating agent, subjecting an article to be treated to the surface treatment with the pre-treating agent and then subjecting the pre-treated article to electroless plating. The article can have a mirror surface, such as a semiconductor wafer.

WO '898 has been cited by the Examiner as disclosing a desirable pre-treatment agent for providing palladium on a surface with a mirror finish, such as a semiconductor wafer, by using a pretreatment agent containing a noble metal reacted or mixed in advance with a silane coupling agent having a functional group with metal-capturing capability. However, since the primary Kondo et al reference is concerned with the plating of an article having a roughened surface, WO '898 does

not cure the deficiencies with respect to the combination of Kondo et al, Uzoh et al and Maenosono discussed above. As such, it is respectfully submitted that the combination of Kondo et al, Uzoh et al, Maenosono and WO '898 does not even present a showing of prima facie obviousness under 35 USC 103(a).

The objective evidence of record in the present application further supports the patentability of currently presented Claim 6. On pages 10-14 of the present specification, seven Examples according to the present invention and three Comparative Examples are presented. · Comparative Example 1, only formalin was used as a reducing agent. In Comparative Example 2, glyoxylic acid was the only reducing agent. In Comparative Example 3, the stabilizer for inhibiting copper deposition was not provided in the electroless copper plating solution. As shown by the results of Comparative Examples 1-3, the comparative electroless copper plating solutions produced inferior results. present invention, it is believed that the application of a noble metal/silane pretreatment agent having a functional group with a metal-capturing capability allows a palladium catalyst to be uniformly and firmly adhered to the mirror surface and, when the pretreated mirror surface is treated with the plating solution of the present invention, the second reducing agent, which has a higher activity, acts on the cupric ions, initiates uniform copper deposition in a first phase and then the additionally deposited copper activates the first reducing agent to thereby improve the copper uniformity. The stabilizer prevents excessive deposition reactions and allows a uniform plating at lower temperatures to be achieved, even on a mirror surface, on which a plating reaction hardly occurs. Given the unexpected benefits associated with the invention defined by Claim 6, it is respectfully submitted that Claim 6 is patentably distinguishable over the prior art cited by the Examiner.

# REJECTION OF CLAIM 5 UNDER 35 USC 103(a) OVER KONDO ET AL IN VIEW OF UZOH ET AL, MAENOSONO AND WO '898 AND

FURTHER IN VIEW OF YOSHIDA ET AL AND VERBUNT
Claim 5 limits Claim 6 in requiring that the first
reducing agent is glyoxylic acid, the second reducing agent is
hypophosphorus acid and the stabilizer to inhibit copper
deposition is 2,2'-bipyridyl. Appellants arguments advanced
above with respect to Kondo et al, Uzoh et al, Maenosono and
WO '898 are hereby incorporated by reference herein with
respect to the rejection of Claim 5.

The Yoshida et al reference discloses an electroless copper plating bath containing a cupric compound, a cupric ion complexing agent, a reducing agent and a pH adjusting agent, in which a carboxylic acid is added as a reaction accelerator to accelerate the oxidation reaction of the reducing agent. The Examiner has cited this reference as teaching that when providing copper electroless plating solutions, it is known to exchange formalin for glyoxylic acid as a reducing agent to provide a less problematic material, that glyoxylic acid has a structure similar to formalin and is believed to have an oxidation reaction mechanism similar to formalin.

The Verbunt reference discloses a copper bath composition containing water, copper ions, hydroxide ions, a complexing agent to inhibit the formation of copper oxides, copper hydroxides and copper salts, a stabilizer to reduce the rate of electroless copper plating, a reducing agent to promote the electroless reduction of the copper ions to copper metal and a catalyst to promote the electrolytic reduction of copper ions to copper metal. This reference has been cited by the Examiner as teaching that when providing copper electroless plating solutions, it is well known to provide hypophosphite in the form of sodium hypophosphite or to provide the hypophosphite from hypophosphorus acid.

Verbunt and Yoshida et al do not cure the deficiencies contained in the previously discussed Kondo et al, Uzoh et al,

Maenosono and WO '898 references. That is, Yoshida et al and Verbunt in combination with the previously discussed references do not present a showing of prima facie obviousness under 35 USC 103(a) with respect to currently presented Claim 5 and, moreover, given the evidence of unobviousness with respect to Claim 5 in the present specification shown in Example 2 of the present specification, even if a proper showing of prima facie obviousness of Claim 5 was made, the objective evidence further establishes the patentability of presently presented Claim 5.

#### CONCLUSION

For the reasons advanced above, it is respectfully submitted that Claims 5 and 6 are patentably distinguishable over the prior art cited by the Examiner. Reversal of the Examiner is respectfully solicited.

Respectfully submitted,

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Encl: Claims Appendix
Evidence Appendix
Related Proceedings Appendix
Postal Card

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# CLAIMS APPENDIX

- 5. An electroless copper plating method according to Claim 6, wherein the first reducing agent is glyoxylic acid, the second reducing agent is hypophosphorous acid and the stabilizer to inhibit copper deposition is 2,2'-bipyridyl.
- 6. An electroless copper plating method comprising the steps of:

preparing a pretreatment agent by reacting or mixing a noble metal compound and a silane coupling agent having a functional group with metal-capturing capability;

pretreating a mirror surface having a surface roughness of less than 10 nm with the pretreatment agent prior to electroless copper plating;

performing electroless copper plating on the pretreated mirror surface with an electroless copper plating solution comprising a first reducing agent, hypophosphorous acid or a hypophosphite as a second reducing agent and a stabilizer for inhibiting copper deposition; and

forming a thin film having a thickness of no more than 500 nm on the pretreated mirror surface by the electroless copper plating.

# EVIDENCE APPENDIX

There is no extrinsic evidence relied upon by Appellants in the appeal.

# RELATED PROCEEDINGS APPENDIX

There are no related proceedings with respect to the present application.